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Paul S. Bagus

and

Charles W. Bauschlicher, Jr.

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Paul S. Bagus

IBM Research Laboratory

Charles W. Bauschlicher, Jr.

Institute for Computer Applications in Science and Engineering

ABSTRACT

The free ion 1s binding energy shifts for oxygen anions are investigated as a function of charge of the anion. The ΔSCF method is used for the calculation of the binding energies. In order to have results applicable to oxygen in bulk ionic oxides, the $O^=$ anion in the configuration $1s^2 2s^2 2p^6$ is studied. It is shown that the restricted Hartree-Fock method cannot lead to meaningful results for a free $O^=$ anion. The anion must be stabilized by an external potential. We have used a Watson sphere for this potential and obtained binding energies for several fractional charge states between O^0 and $O^=$. At O^0, we find that the binding energy shift is 18 eV/electron; at $O^=$, it is 12 eV/electron. Our "free" ion $O^=$ binding energy plus the ionic point charge Madelung potential for FeO gives a binding energy $\sim$3eV larger than the observed value.

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The chemical shifts of the core level binding energies observed in x-ray photoemission, XPS, provide information on the chemical environment and bonding of atoms in molecules and solids.[1,2] In particular it is useful to interpret these chemical shifts in terms of the effective ionicity or charge state of the atom. This is often done by using empirical or semiempirical approaches which divide the shift into an intra-atomic or free ion part and a part due to the potential generated by the environment (or surrounding atoms).[1-3] Although such approaches do not explicitly take into such effects as extra atomic final state relaxation,[4-6] they have been used with reasonable success in a wide range of applications.

The interpretation of the O 1s binding energies for oxygen in bulk metal oxides is a case of particular concern. For insulating ionic oxides (e.g., NiO, MnO, or SrO), O is normally assigned a formal change of 2- . The O^{2-} anion, which is unstable as a free ion, is described as being stabilized by the Madelung potential of point changes representing the cations (metal) and anions (oxygen).[7,8] The usual analysis of the O 1s binding energy would require that we consider four terms in order to determine the effective change of these O anions as "observed" by XPS: (1) the "free ion" 1s binding energy of $O^{=}$; (2) the contribution of the Madelung point charge potential; (3) a term taking account of the overlap and exchange repulsion of the extended change distributions about the anions and cations;[9,10] and (4) the contribution of extra-atomic final state relaxation.[4-6] Parry,[10] for example, has proposed a relationship which for the 1s binding energy of O in a compound, $B_{comp}(O_{1s})$, may be cast in the form:

$$B_{comp}(O_{1s}) = B(O_{1s}, \text{free atom}) + \lambda q_o + \sum_{c \neq o} q_c / R_{oc} + \sum_{c \neq o} \Delta c\,(R_{oc})\{N_c\} \qquad (1)$$

Here $B(O_{1s}$, free atom) is the 1s binding energy of a free O atom; q_o is the effective charges on one O ion (the atom to be ionized) and q_c the charge on any other anion or cation in the system; R_{oc} is the distance of the ion c from the O ion; $\Delta_c(R_{oc})$ is a term to account for the overlap of charge of ion c with the O ion and depends on the distance R_{oc}; N_c is the number of valence electrons on the c^{th} anion or cation; and λ is the free ion binding energy shift assumed to be constant for all possible charges on the ion. The term λq_o is the free ion shift; the first summation is the Madelung potential at oxygen and the second summation reflects the fact that the charge distributions of the other ions overlap that of the oxygen atom. Thus, Parry's formula includes all of the contributions described above except the fourth due to final state relaxation.

In order to determine the validity of this sort of decomposition of the chemical shifts, it is necessary to obtain reliable values for the various contributions discussed above for at least a few representative cases.

In this paper, we are concerned with an accurate determination of the free ion shift λ. This is done by computing ΔSCF[11] 1s binding energies for O in various charge states, including fractionally charged anions, up to $O^{=}$. The ΔSCF method gives rather accurate 1s binding energies,[1,3,11] hence it can be expected to give reliable values for λ.

In fact, since it is difficult or impossible to obtain experimental values of 1s binding energies of free ions and often for neutral atoms, the ΔSCF method offers the best way to obtain accurate values for λ.

We shall first consider the nature of the restricted Hartree-Fock (RHF) solution for a free $O^{=}$ anion with configuration $1s^2 2s^2 2p^6$. We shall show that it is impossible to obtain meaningful results for $O^{=}$ without imposing some sort of external potential. We then describe a procedure first used by Watson[12] for placing the atom in the potential of a charged sphere and report ΔSCF 1s binding energies for several charge states of O using the charged sphere. A value of λ is derived from these calculated binding energies.

Several workers[13,14] have reported basis set RHF Self Consistent Field, SCF, wave functions for $O^{=}$ $(1s^2 2s^2 2p^6)$. They find an energy for $O^{=}$ which is about 8 eV higher than that for the ^3P $(1s^2 2s^2 2p^4)$ ground state of neutral O. This would appear to confirm the fact that free $O^{=}$ is unstable. However, the 2p orbital energy, ϵ_{2p}, is greater than zero; Huzinaga and Hart-Davis[14] find $\epsilon_{2p} = +0.066$ hartree $= +1.8$ eV. Positive orbital energies are appropriate for continuum orbitals yet the basis set used forces the 2p orbital, θ_{2p}, to be discrete and square integrable. It is necessary to use a more flexible basis set to resolve this contradiction and obtain a meaningful wave function for $O^{=}$. It would seem that one of two things must happen when a more flexible basis is used. Either ϵ_{2p} becomes negative as is required for a discrete square integrable orbital or the 2p orbital becomes a continuum electron, denoted ϵ_p, and we obtain a solution for $O^{+4}(1s^2 2s^2)$ + six free electrons. Since the energy of O^{+4} is 6.55 hartrees = 178 eV above that of neutral O, this second possibility seems to be ruled out.

In order to investigate the nature of free $O^=$ more closely, a series of SCF calculations were performed. Starting from the 5s 3p Slater type (STO) $O^=$ basis set of Ref. 14 a diffuse 2p function was added, then all other 2p exponents were optimized for $O^=$. The range of the exponent of the diffuse function was 0.07 to 0.01. The total SCF energy, the 2p orbital energy, and the coefficient of the diffuse exponent are shown in Table I for several values of the diffuse p exponent. The values of ϵ_{2p} are all positive but have become small and decrease almost linearly with the value of the diffuse exponent. The total energy, E_{SCF}, is also decreasing almost linearly with the value of the diffuse exponent. For an exponent value of zero (a continuum electron with zero kinetic energy), linear extrapolation gives an ϵ_{2p} of 0 and a total energy above that of O^- ($1s^2 2s^2 2p^5$) by 0.26 hartree = 6.9 eV and above that of O(3P) by 0.28 hartree = 7.5 eV. However, the coefficient of the diffuse p basis has a limiting value of .37 for zero exponent. This indicates that the 2p orbital has two distinct parts, an inner or bound part going through a maximum at $\sim$0.9 bohr and decreasing to 0 at $\sim$14 bohrs and an outer or free electron part.

The square of the free electron coefficient, $(.37)^2 = .14$, leads to a total of $0.82 = 6 \times 0.14$ continuum electrons in the $2p^6$ configuration. Thus we have, within the restrictions of the RHF model, come very close to describing O^- plus a free electron. However, we have done this in a rather special way which can be seen clearly if we write the 2p orbital as

$$2p = A\, p_d + B\, p_c \quad ; \qquad (2)$$

where p_d represents the discrete part of the 2p orbital and p_c the continuum part. We may now expand the closed shell RHF $2p^6$ configuration as

$$2p^6 = A^6 p_d^6 + 6A^5 BC_1 p_d^5 p_c^1$$

$$+ 15A^4 B^2 C_2 p_d^4 p_c^2 + \cdots B^6 p_c^6 \; ; \qquad (3)$$

where the coefficients C_1, C_2, $\cdots$, C_5 are determined from angular momentum coupling considerations.[15] We can see clearly that the RHF wave function is a superposition of states with different numbers of continuum electrons. This indicates that calculations on free $O^=$ are meaningless, since with a flexible basis set one is computing a wave function which is a combination of $O^=$, $O^- + e$, $O + 2e^- \cdots O^{+6} + 6e^-$ and the system is becoming $O^- + e^-$ as much as possible within the RHF model.

We therefore decided to adopt the approach of Watson[12] and stabilize $O^=$ with a charged sphere. (We actually computed oxygen surrounded by six point charges placed to give the system overall O_h symmetry. For an atom with only s and p orbitals this is identical to using a charged sphere.)

Separate self-consistent-field (SCF) calculations were performed for both the parent and 1s hole species; the 1s binding energy is obtained as the difference of the total SCF energies for parent and hole state. This ΔSCF procedure takes into account the intra-atomic final state relaxation effects and yield accurate values of atomic and molecular one level binding energies.[3,4,11] A contracted gaussian basis (9s5p/4s 3p) set, optimized for O^-, was employed. (The choice of this basis set in an atomic calculation was made to allow easy comparison with ab initio SCF cluster model studies of ionic transition metal oxides using this basis set, e.g., FeO[16], NiO[17] and CoO[18].)

In order to assess the effects of the charged sphere, it was initially eliminated and SCF calculations were performed for the parents $O(^3P)$ and $O^-(^2P)$ and both of the possible 1s hole states in which the p coupling of the parent was retained. The results are summarized in Table II under "no field." The weighted average of the 1s binding energy for $O(^3P)$ (2/3 the BE for a ^4P hole state plus 1/3 the ^2P BE) is 545.7eV. This is remarkably close to the Hartree-Fock limit value of 545.0eV obtained by Bagus and Schaefer[4] with an extended basis set of STO's.

The $O^{=}_{1s}$ binding energy was calculated within the charged sphere, along with a repetition of all other oxygen calculations. The distance and magnitude of the charge were varied. The parameters adopted for the remainder of this work are a charge of +2 at a distance of 3 bohrs from the oxygen nucleus. This specific field was chosen because it reproduced the no field 1s binding energies of O and O^- to within 1eV. Besides, the results are fairly insensitive to the choice of the field. (Watson[12] used a slightly smaller sphere radius of 2.66 bohrs.) The results of these calculations are tabulated in Table II under "with field." The total radial charge density for $O^=$ was tabulated and from this we estimate .1 electrons are outside of the charged sphere.

The calculation of the binding energy in this charged sphere requires a correction to the difference in total energies since the total charge within the sphere changes by 1. Assuming no overlapping of charge, we used a simple electrostatic correction. The .1 electrons outside of the sphere indicates this is not exactly true. Some measure of this effect can be seen from the difference between the no field and with field 1s binding energies of O and O^-. As can be seen in Table II

the O binding energies change by .3 ev while the O^- has a change of .8 ev. The effect increases with increased charge on the oxygen since the larger size of the anion causes a greater overlapping with the charged sphere. The size of the error is small and should not adversely effect our results.

The shape of the 1s binding energy vs total charge is of interest and is not well determined by only 3 points. However, if an average of configurations[9] formalism is adopted, non-integral number of electrons can be treated. The 1s binding energy was calculated from $O^=$ to O at intervals of .25 electrons. The results are summarized in Table III and plotted in Figure 1. From these results we can obtain a value for the binding energy shift λ in Eq. (1). It is clear that λ is not quite constant with the change q of the parent, O^{-q}, but varies from 12 eV electron at O^{-2} to 18 eV/electron at O^o. More important, these values are substantially smaller than the semi-empirical value of $\lambda = 30.4$ eV/electron obtained by Parry[10] and used by him for an analysis of the effective ionicities in various lead oxides. Our values, which are substantially smaller than Parry's, would probably lead, using his analysis, to different (larger) ionicities for the lead oxides.

It is also interesting to examine the effect of the Madelung potential on the O_{1s} binding energy in one representative case, that of FeO. The Madelung potential at the O site, assuming +2 (cation) and -2 (anion) charges is 23.3 eV obtained using the lattice parameters given by Wyckoff.[20] The O_{1s} binding energy for O^{-2} in this potential is 538.5 eV (= 515.2 + 23.3) and is referenced to vacuum. The observed[21] XPS binding energy in FeO, referenced to the Fermi level, (E_F), is 530.1 eV. Taking $\sim$5 eV as a rough estimate of the work function, we have the observed value with respect to vacuum as 535 eV which is not too far from our calculated 538.5 eV. It is easy to imagine that effects due to

charge overlap or final state extra-atomic relaxation could account for the difference. However, it would be quite important to demonstrate that this is indeed the case.

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Table I. Summary of free $O^{=}$. For each choice of the diffuse 2p exponent. The total energy, the 2p orbital energy (both in hartrees), and the coefficient of this diffuse function in the 2p orbital are given.

Exponent	Total E	ϵ_{2p}	Coefficient
0.07	-74.520034	+0.02745	0.369494
0.06	-74.523649	0.02422	0.360212
0.05	-74.525520	0.02018	0.361756
0.04	-74.527467	0.01613	0.363135
0.03	-74.529499	0.01209	0.364321
0.02	-74.531622	0.00805	0.365238
0.01	-74.533831	0.00401	0.366002
0.0 (extrapolated)	-74.534	0	0.37

Table II. 1s binding energy for O, O^- and $O^=$. The binding energies are reported in eV. The column labelled "no field" summarizes the results without the charged sphere.

Parent	1s hole state	No field	With field
O	^2P	548.8	548.5
O	^4P	544.2	543.9
O^-	^1P	530.9	530.1
O^-	^3P	528.3	527.2
$O^=$	^2S	———	515.2

Table III. 1s binding energy for O^{-q} using the average of configurations. All binding energies are in eV and all calculations were performed using the charged sphere.

Parent	Binding energy
O	545.4
$O^{-.25}$	540.9
$O^{-0.5}$	536.3
$O^{-0.75}$	532.1
$O^{-1.}$	527.9
$O^{-1.25}$	524.5
$O^{-1.5}$	521.2
$O^{-1.75}$	518.1
$O^{-2.0}$	515.2

Figure 1. A plot of the 1s binding energy vs charge (q) on the O^{-q} parent. The calculations used the average of configurations and a charged sphere.